DETERMINATION OF TIN BY LONG ABSORPTION CELL-ATOMIC-ABSORPTION SPECTROPHOTOMETRY FOLLOWING STANNANE GENERATION

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The increasing importance of determining trace elements in natural water, soil, sediment, plant and food has created a need for rapid and accurate methods of measurement. Tin in at least small quantity is present in these and other materials when analyzed by suitably sensitive methods. However, tin determinations are often ignored largely because of the lack of sufficiently, sensitive analytical techniques for measurements at levels less than 1 ppm.

Conventional atomic-absorption methods for tin determination have disadvantages, such as low sensitivity and chemical interference. Recent developments in hydride generation methods coupled with atomic-absorption have made the study of this element feasible.

Reports (1–9) have appeared on the development and application of the hydride generation technique, using sodium borohydride as a reducing agent, for elements that readily form volatile hydrides. Some of these investigators (1, 2, 4, 7) have made tin determination. However, only two reports (4, 7) have described some interference with sodium borohydride ($NaBH_4$) reduction. Moreover, tin was determined by a hydride generation-flameless atomic-absorption spectrophotometric technique with thermal atomization (1, 7). The principal advantage of this flameless technique has been its high sensitivity, but it has poor reliability because of pressure changes in the absorption cell from extra hydrogen evolved during hydride generation.

Consequently, the author investigated the use of a long absorption cell fitted with a hydride inlet in a nitrogen-hydrogen flame system, and improved the sensitivity, reproducibility, and the linearity of the calibration curve for atomic-absorption spectrophotometric determinations of tin.

The present paper describes investigations on optimal conditions for rapid, sensitive tin determination with stannane (tin hydride, SnH_4) generation-atomic-absorption spectrophotometer equipped with a long absorption cell, and the application of this technique to determination of tin dissolved in canned fruit juices.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash, Model AA-1 Mark II, atomic-absorption spectrophotometer equipped with a Jarrell-Ash tin hollow-cathode lamp and a custom-made silica long absorption cell (60 × 1.2 cm i.d.) fitted with a hydride inlet (3 mm i.d.) was utilized with a Beckman burner supplied with nitrogen and

hydrogen.

The apparatus used for hydride generation was a modified Nippon Jarrell-Ash, Model ASD-1A, hydride measurement unit coupled to a hydride generating cell approximately 40 m*l* in volume. The analytical system was similar to that described for arsenic determination (10).

Reagents

Analytical reagent-grade chemicals and deionized-distilled water were used to prepare all solutions throughout the experiment. Standard tin solutions were freshly prepared by diluting stock solutions before use.

Tin(IV) stock solution (1 mg ml^{-1}). High-purity tin metal (500 mg) was dissolved in 40 m*l* of concentrated sulfuric acid by heating. After cooling, dilution followed to 500 m*l* with 2 N hydrochloric acid.

Tin(II) stock solution (1 mg ml^{-1}). Stannous chloride dihydrate (950 mg) was freshly dissolved in 50 m*l* of concentrated hydrochloric acid and diluted to 500 m*l* in 2 N hydrochloric acid.

Sodium borohydride solution (5 w/v %). Sodium borohydride was freshly dissolved in 0.1 N sodium hydroxide solution.

Procedures for tin determination

Freshly prepared 5 w/v % sodium borohydride solution (1 m*l*) was transferred into a stannane-generating cell, and the cell attached to the apparatus. The needle of the plastic syringe containing 1 m*l* sample solution with less than 0.10 μg of tin was inserted through the side-arm seal of the cell. The four-way stopcock of the apparatus was turned to the sweep position to introduce nitrogen

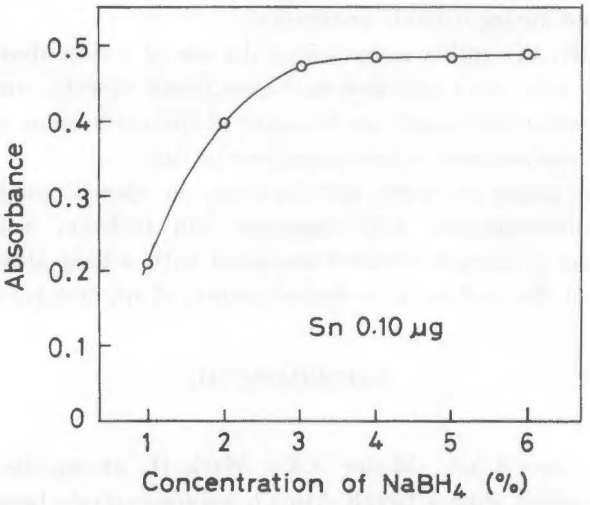

Fig. 1. Effect of sodium borohydride concentration on the evolution of stannane (1 m*l* solution).

into the system, and the sample injected into the cell. The stannane thus generated was swept into the long absorption cell with the nitrogen so that it was atomized in the nitrogen-hydrogen flame, and the absorption signal was recorded. The stopcock was returned to the by-pass position. The cell was carefully rinsed with distilled water and recharged with sodium borohydride solution for the next sample.

The atomic-absorption equipment was operated under the following conditions: wavelength, 286.3 nm; lamp current, 8 mA; gas flow-rates, nitrogen 1.5, hydrogen 1.5 and auxiliary nitrogen 6 l min^{-1}; slit (spectral band width), 1 nm.

RESULTS AND DISCUSSION

Required concentration of sodium borohydride

The effect of sodium borohydride concentration on the evolution of stannane was investigated. Figure 1 shows that the use of more than 3 w/v % sodium borohydride concentration (1 ml volume) can quantitatively reduce up to 0.10 μg of tin(IV) to stannane. In the work here, 1 ml of 5 w/v % sodium borohydride solution was used.

Effect of flow-rate of carrier gas

The optimum condition for tin sensitivity was dependent on the flow-rate of auxiliary nitrogen, as shown in Fig. 2. Tin absorbance increased with the increasing flow-rate of auxiliary nitrogen up to 6 l min^{-1} when flow-rates of nitrogen and hydrogen were both 1.5 l min^{-1}. A stable, optimum sensitivity was obtained with flow-rate of auxiliary nitrogen between 6 and 8 l min^{-1}; a flow-

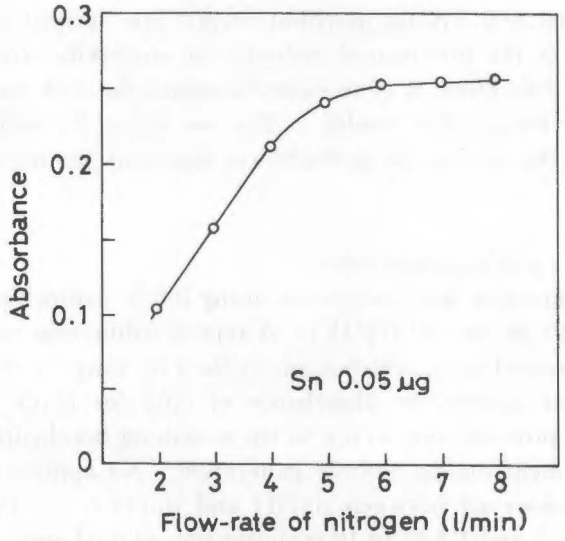

Fig. 2. Effect of nitrogen flow-rate on the evolution of stannane (1 ml solution).

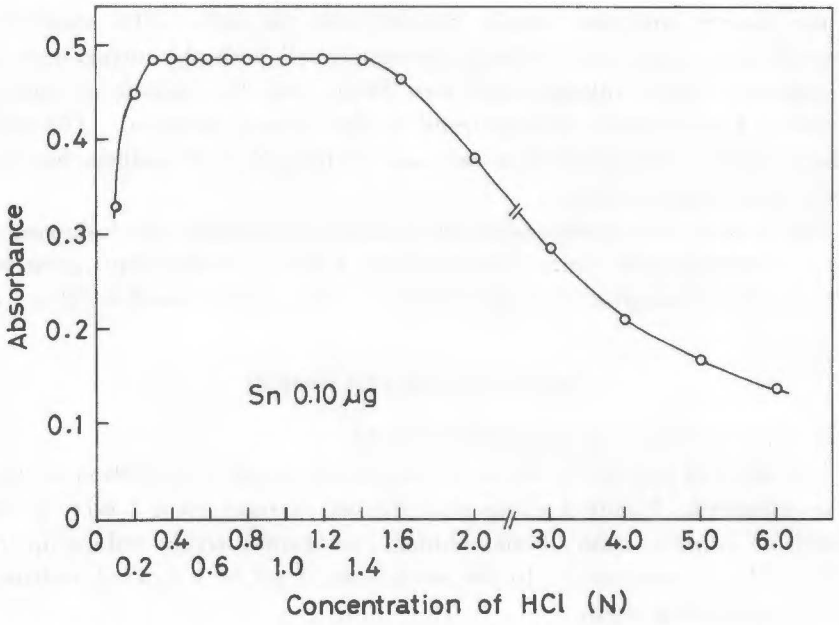

Fig. 3. Effect of hydrochloric acid concentration on the evolution of stannane (1 *ml* solution).

rate of auxiliary nitrogen of 6.0 l min^{-1} was used throughout this study.

Influences of inorganic acid concentrations

The effect of inorganic acids on stannane generation was investigated. The results are shown in Figs. 3 and 4. The optimum range of acid concentrations was: 0.3–1.4 N for hydrochloric acid, 0.4–1.2 N for nitric acid, 0.4–1.3 N for sulfuric acid and 0.3–0.7 N for perchloric acid. The optimal concentrations are critical because of the pronounced decrease in sensitivity with increasing acid concentrations. Therefore, it is necessary to adjust the acid concentration of the sample carefully for reliable results. The use of tin(II) solution gave similar results. Thus, the acidity of hydrochloric acid was maintained at 0.6 N in further studies.

Calibration curve and reproducibility

A calibration curve was constructed using 0.6 N hydrochloric acid solutions containing 0–0.10 μg ml^{-1} of tin(IV). A typical calibration curve for tin determination is shown in Fig. 5, which is linear for a tin range of 0–0.10 μg ml^{-1}. In this measurement system, an absorbance of 0.01 for blank solution was observed. This is probably due to not to tin in sodium borohydride but mainly to hydrogen enrichment during hydride generation. No appreciable difference in sensitivity was observed between tin(II) and tin(IV). The coefficients of variations were 1.5 and 1.4 % in 10 replicate runs of 0.04 and 0.08 μg ml^{-1} of tin (IV), respectively.

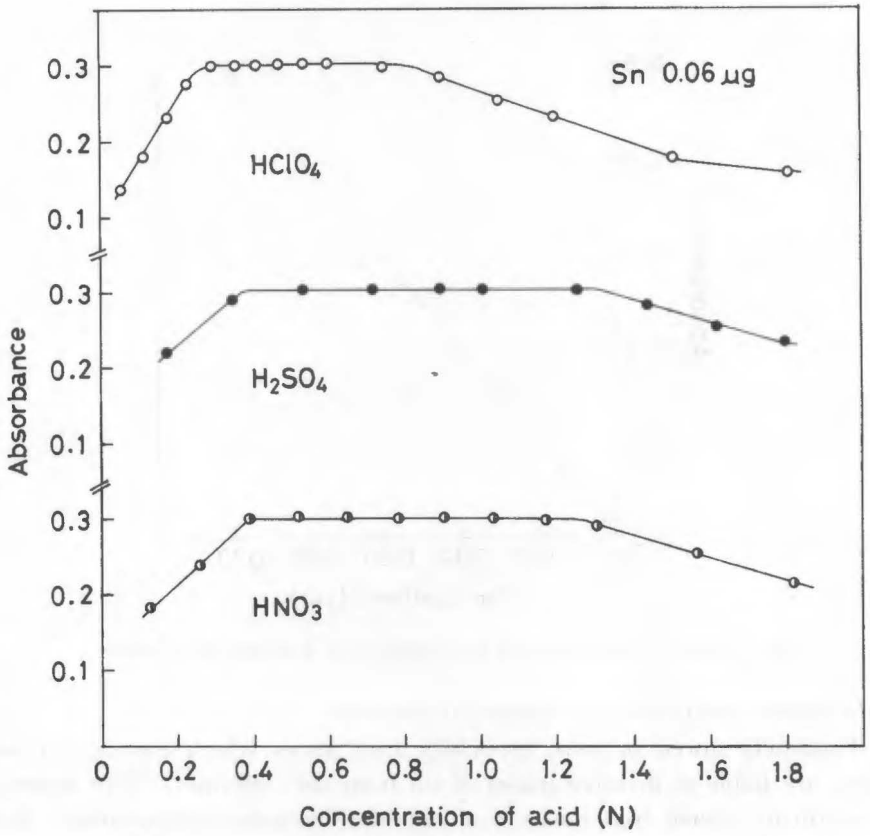

Fig. 4. Effect of perchloric, sulfuric and nitric acid concentrations on the evolution of stannane (1 m*l* solution).

Effect of foreign ions

The effect of diverse ions on determinations of 0.10 μg ml^{-1} of tin(IV) was examined by the proposed procedure. The following ions did not interfere with stannane generation at 100 μg ml^{-1}: sodium, potassium, calcium, magnesium, barium, strontium, cadmium, zinc, manganese(II), aluminum, iron(III), chromium(III, VI), vanadium(V), lead, chloride, sulfate, nitrate, silicate and phosphate. The maximum permissible amounts of other ions were as follows: molybdenum(VI) 60 μg ml^{-1}, mercury(II) and tellurium(IV) 40 μg ml^{-1}, selenium(VI) and silver 20 μg ml^{-1}, copper(II) 6 μg ml^{-1}, bismuth(III), cobalt(II) and antimony(III) 10 μg ml^{-1}, copper(II) 6 μg ml^{-1}, arsenic(III, V) 5 μg ml^{-1}, selenium(IV) 4 μg ml^{-1}, and nickel(II) 0.2 μg ml^{-1}. Therefore, nickel(II) and hydride-forming elements, such as selenium(IV), arsenic(III, V), antimony(III) and bismuth(III) showed a relatively strong effect on stannane generation.

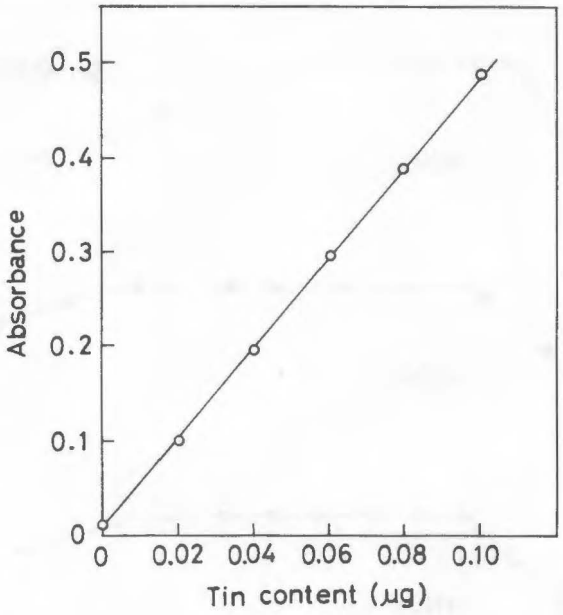

Fig. 5. Typical calibration curve for determination of tin in 1 m*l* of solution.

Application to tin dissolved in canned fruit juice

Foodstuffs stored in cans, especially fruit juices which contain a residual acidity, are liable to dissolve traces of tin from the container. The determination of tin in canned fruit juices is of considerable public importance. Therefore, the development of a rapid and sensitive determination method for tin in canned fruit juices is desirable.

The determination of tin in canned juice by atomic-absorption spectrophotometry has been described by several authors (11, 12, 13). However, conventional atomic-absorption methods for tin using nitrous oxide-acetylene or air-acetylene flame have low sensitivity. Okada *et al.* (12) improved the sensitivity for tin determination using T-shaped, long absorption tube, compared with the conventional atomic-absorption method. Amakawa *et al.* (13) reported the determination of tin in soft drinks by flameless atomic absorption spectrophotometry, using a graphite tube following coprecipitation with zirconium hydroxide.

The proposed method using hydride generation technique was used to determine tin dissolved in canned fruit juices.

The procedure was as follows: Immediately after opening a can, the contents were transferred into a beaker and then filtered through Toyo No. 5A filter paper. A 1 m*l* portion of sample was transferred into a 50 m*l* volumetric flask, 5 m*l* of concentrated hydrochloric acid was added, and the sample was diluted to the indicated point with water. The prepared solution was further diluted to adjust the tin concentration at 0.6 N hydrochloric acid to within the

TABLE 1

Determination of tin in canned fruit juices

Sample [a]	Tin added (μg)	Tin found (μg)	Tin recovered (μg)	Recovery (%)	Tin in sample (μg ml^{-1})
Orange juice	None	21.2			21.2
	8.0	29.4	8.2	103	
	16.0	36.6	15.4	96	
Tomato juice	None	12.3			12.3
	8.0	19.8	7.5	94	
	16.0	27.4	15.1	94	
Peach juice	None	12.5			12.5
	8.0	20.7	8.2	103	
	16.0	28.6	16.1	101	
Mixed juice	None	10.4			10.4
	8.0	18.5	8.1	101	
	16.0	25.5	15.1	94	
Peach syrup	None	45.4			45.4
	20.0	65.0	19.6	98	
	40.0	85.7	40.3	101	

[a] Sample taken, 1 m*l*.

optimum range of standard solutions, and then analyzed.

The results are presented in Table 1. The tin concentrations found in five kinds of juices were: 21.2, 12.3, 12.5, 10.4 and 45.4 μg ml^{-1} in orange, tomato, peach, mixed and peach syrup, respectively. Recovery was determined by the addition of known amounts of tin to the canned fruit juices. Tin recoveries were within the 94 – 103 % range. Thus, by simply diluting canned fruit juice, tin content can be successfully determined.

SUMMARY

A method is reported for rapid, sensitive and reliable tin determination by atomic-absorption spectrophotometry *via* hydride generation using sodium borohydride as a reducing agent. A long absorption cell (60 × 1.2 cm i.d.) apparatus fitted with a hydride inlet and a nitrogen-hydrogen flame system was applied to enhance the sensitivity and reliability of tin measurement. The effects of inorganic acids, sodium borohydride concentrations, flow-rate of auxiliary nitrogen and foreign ions were examined systematically. The optimal concentrations of inorganic acids were: 0.3–1.4 N, 0.4–1.2 N, 0.4–1.3 N and 0.3–0.7 N for hydrochloric, nitric, sulfuric and perchloric acid, respectively. The calibration curve obtained was linear up to 0.10 μg of tin (1 m*l* sample). No appreciable difference in sensitivity was observed between tin(II) and tin(IV). The coefficients of variations were within 1.5 % in determinations of 0.04 and 0.08 μg ml^{-1} of tin. The procedure described was satisfactory for tin dissolved in

canned fruit juices.

ACKNOWLEDGMENT

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